Synthesis of hetaryl-substituted 1,2,4-trithiolanes via a three-component reaction with dihetaryl thioketones, benzyl azide, and 2,2,4,4-tetramethyl-3-thioxocyclobutanone

Mlostoń, Grzegorz ; Celeda, Malgorzata ; Linden, Anthony ; Heimgartner, Heinz

Abstract: The three-component reactions with a hetaryl thioketone, 2,2,4,4-tetramethyl-3-thioxocyclobutanone, and excess benzyl azide performed at 60°C in the presence of LiClO4 lead to the formation of two types of 1,2,4-trithiolanes. As the major products, the non-symmetrical dihetaryl-substituted spiro-1,2,4- trithiolanes are formed. In addition, the symmetrical dispiro-1,2,4-trithiolane is identified. These products are formed in competitive [3 + 2] cycloadditions of the in-situ-generated thiocarbonyl S-sulfide with the thioketones used in the reaction.

DOI: https://doi.org/10.1080/17415993.2015.1082182

JSC (M-322) revised

Synthesis of hetaryl-substituted 1,2,4-trithiolanes via a three-component reaction with dihetaryl thioketones, benzyl azide and 2,2,4,4-tetramethyl-3-thioxocyclobutanone

Grzegorz Mlostoń[a*], Małgorzata Celeda[a], Anthony Linden[b] and Heinz Heimgartner[b]

[a]*Department of Organic and Applied Chemistry, University of Łódź, Tamka 12, PL-91-403 Łódź, Poland;* [b]*Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland*

Abstract

The three-component reactions with a hetaryl thioketone, 2,2,4,4-tetramethyl-3-thioxocyclobutanone, and excess benzylazide performed at 60 ºC in the presence of $LiClO_4$ lead to the formation of two types of 1,2,4-trithiolanes. As the major products, the non-symmetrical dihetaryl-substituted spiro-1,2,4-trithiolanes are formed. In addition, the symmetrical dispiro-1,2,4-trithiolane is identified. These products are formed in competitive [3+2] cycloadditions of the in situ generated thiocarbonyl *S*-sulfide with the thioketones used in the reaction.

Graphical Abstract

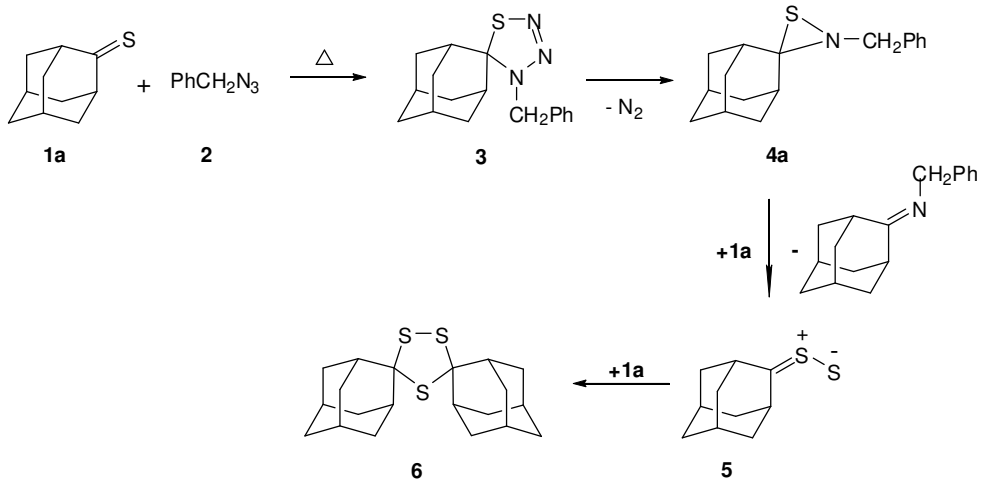
Keywords: thioketones; organic azides; [3+2] cycloadditions; thiocarbonyl *S*-sulfides; sulfur heterocycles

1. Introduction

Among five-membered poly-sulfur heterocycles, 1,2,4-trithiolanes constitute an important class of compounds. Some of them, e.g., the parent 1,2,4-trithiolane and its

3,5-dialkyl-substituted derivatives are widely spread in nature. The parent compound was isolated as the major component from Shiitaki mushrooms (*Lentinus edodes*) [1] and later on also from bitter beans (*Parkia speciosa*).[2] *Cis*- and *trans*-3,5-dimethyl-1,2,4-trithiolane are known as important components in the mixture of sulfur-heterocycles, which determine the flavor of boiled beef meat.[3] The corresponding diethyl derivatives were identified in the composition of common onion (*Allium cepa*) essential oil.[4] Both the parent compound [1] and 3,5-dialkyl 1,2,4-trithiolanes [5] have been prepared by heterocyclization reactions starting with chloroalkanes using Na_2S as the sulfur source. An alternative approach, based on the reaction of ammonia (or a primary amine), H_2S and elemental sulfur, as well as an aliphatic oxo-compound, was developed by Asinger.[6] In recent decades, an elegant method for the preparation of tetrasubstituted 1,2,4-trithiolanes via [3+2] cycloadditions of thioketone *S*-sulfides (thiosulfines) [7] with thioketones was elaborated by Huisgen.[8,9] In that case, the elusive thiosulfines are generated in situ and immediately trapped by the C=S group of the 'superdipolarophilic' thioketone. The Huisgen method for the generation of thiosulfine comprises the transfer of the *S*-atom of a thiirane onto the C=S group.

Some time ago, we reported on a new method for the in situ generation of thiosulfines in the reaction of thioketones with organic azides. Thus, heating of adamantanethione (**1a**) with benzyl azide (**2**) led to dispiro-1,2,4-trithiolane **6** as the [3+2] cycloadduct of adamantanethione *S*-sulfide (**5**) with **1a** (Scheme 1).[10]



Scheme 1

In this reaction, the intermediate thiaziridine **4a** is believed to act as the sulfur donor involved in the generation of the reactive 1,3-dipole **5**. On the other hand, similar reactions of thiobenzophenone (**1b**) with organic azides produce benzophenone imines and not the expected tetraphenyl-1,2,4-trithiolanes.[11]. These results demonstrate the thermolability of the tetraaryl-1,2,4-trithiolanes, which therefore cannot be isolated. Finally, a three-component mixture of an aromatic thioketone, **1a** and an organic azide furnished non-symmetrical 1,2,4-trithiolanes via the [3+2] cycloaddition reaction, and the obtained product is stable enough to be isolated.[10] Aromatic thioketones are more reactive than cycloaliphatic analogues towards organic azides and therefore 3,3-diarylthiaziridines are the sulfur-donating intermediates. Along with **1a**, the sterically crowded 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1c**) is a good model for the synthesis of non-symmetrical 1,2,4-trithiolanes using three-component reactions.[12]

Thiocarbonyl *S*-sulfides were also postulated as reactive intermediates in a multi-step reaction between aromatic thioketone *S*-oxides and **1c** in which some non-symmetrical 1,2,4-trithiolanes were found as the final products.[13]

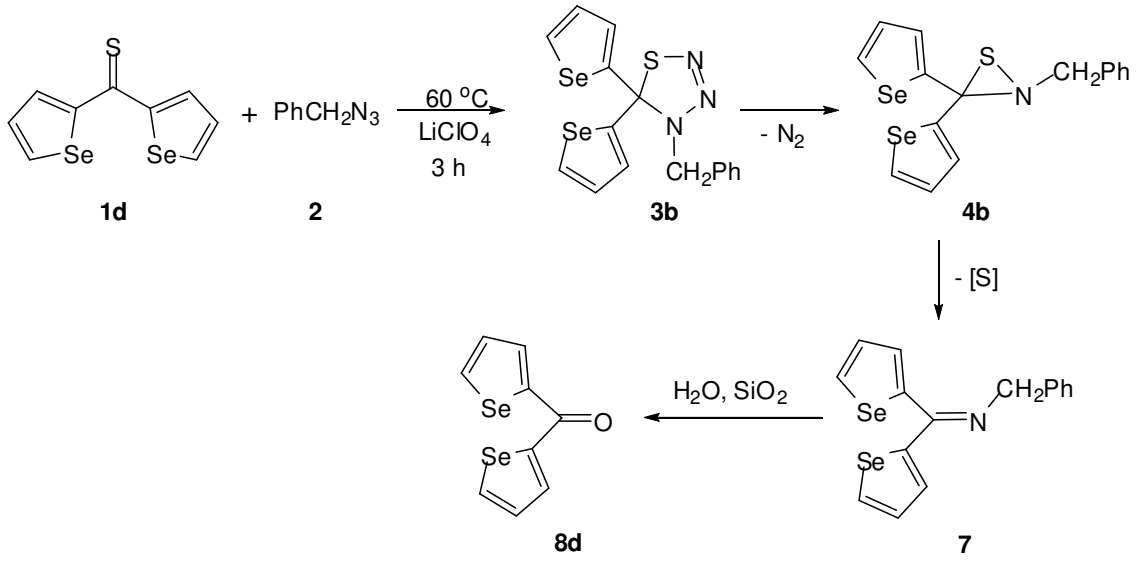
In a recent publication we described a convenient access to differently substituted aryl/hetaryl thioketones.[14] The presence of heteroatoms in the hetaryl ring influences the reactivity of these thioketones significantly, e.g., in [3+2] cycloadditions with diazomethane [15] and with thiocarbonyl ylides.[16] In both cases, the cycloaddition reactions seem to occur via diradical intermediates.

The present study was aimed at testing the reactivity of selected hetaryl thioketones in three-component reactions leading to hetaryl-substituted non-symmetrical 1,2,4-trithiolanes.

2. Results and discussion

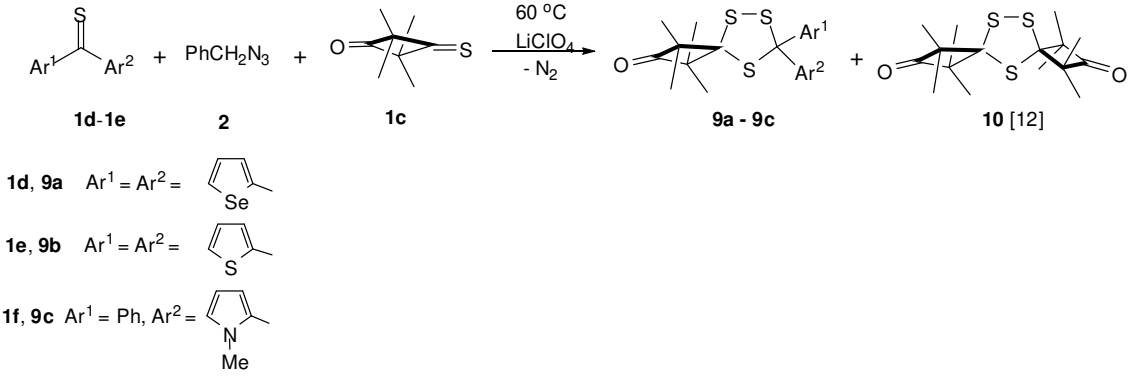
In the test experiment, the reactivity of di(selenophen-2-yl) thioketone (**1d**) toward benzyl azide (**2**) was compared with that of thiobenzophenone (**1b**). The evolution of N_2 from the reaction mixture heated to 80 °C was complete after 4 h, which indicates that **1d** is less reactive then **1b** (80 °C, ca. 2.5 h) in the [3+2] cycloaddition with **2**. When the same reaction was performed in the presence of a catalytic amount of $LiClO_4$, the reaction temperature could be reduced to 60 ºC, and the conversion was complete after 3 h. The crude reaction mixture was separated chromatographically (prep. TLC) and the only product was identified as di(selenophen-2-yl) ketone (**8d**) [14] formed via

hydrolysis of the corresponding *N*-benzylimine **7** (Scheme 2). It is worth of mentioning, that the observed least polar fraction with R_f value ca. 0.9 was attributed to elemental sulfur S_8. This result fits well with that reported for thiobenzophenone (**1b**) [11,17] and indicates that the intermediate dihetarylthiaziridine **4b** can be expected to act as a sulfur donor.



Scheme 2

The three-component reaction with the aromatic **1d** and cycloaliphatic thioketone **1c** in excess benzyl azide (**2**) in the presence of $LiClO_4$ was performed at 60 ºC. In that case, the chromatographic separation of the crude mixture led to a crystalline product (less polar fraction), which in the ^{1}H-NMR spectrum showed two characteristic signals of methyl groups and three multiplets attributed to the selenophen-2-yl substituents. In the IR spectrum, the intense absorption at 1787 cm^{-1} confirms the presence of the cylobutanone unit. Finally, the structure of the spirocyclic 1,2,4-trithiolane **9a** (Scheme 3) was established by X-ray crystallography (Figure 1).



Scheme 3

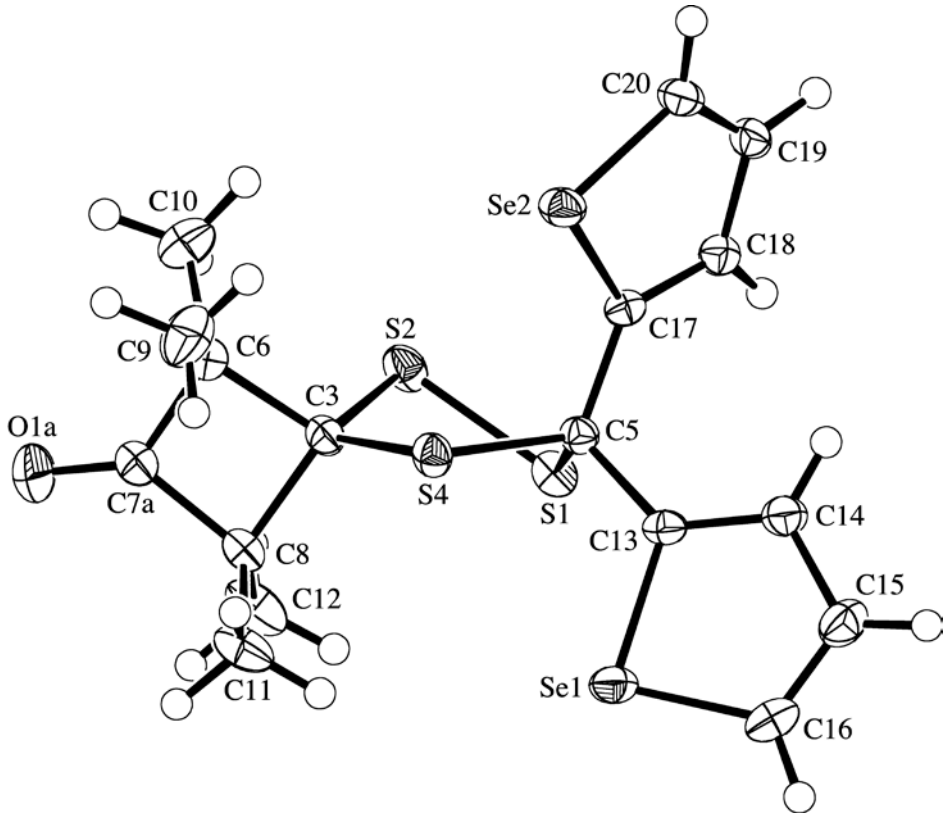


Figure 1. ORTEP plot [18] of the molecular structure of conformation A of **9a** (with 50% probability ellipsoids; arbitrary numbering of atoms)

The more polar fraction isolated after chromatography was identified as a mixture of the known symmetrical dispiro-1,2,4-trithiolane **10** [12] and di(selenophen-2-yl)ketone (**8d**).[14] The analogous experiments with di(thiophen-2-yl) thioketone (**1e**) and *N*-methylpyrrol-2-yl phenyl thioketone (**1f**), respectively, yielded also the desired spiro-1,2,4-trithiolanes **9b** and **9c** side by side with **10** and the corresponding hetaryl ketones **8e**, **f** (Scheme 3).

In an extension of this study, the reaction of diferrocenyl thioketone and benzyl azide (**2**) was tested at 60 ºC. Only after 6 h did the evolution of N_2 cease, but the attempted separation of the complex mixture was unsuccessful. Similarly, the three-component reaction with **1c** led to a complex mixture of non-identified products.

3. Conclusions

The presented study demonstrated that hetarylthioketones are less reactive than thiobenzophenone in [3+2] cycloadditions with benzyl azide, and a catalytic amount of $LiClO_4$ is necessary to reduce the reaction temperature to 60 ºC. In the presence of the sterically crowded 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1c**), mixtures of spiro-1,2,4-trithiolanes **9** containing hetaryl substituents and dispiro-1,2,4-trithiolane **10** are formed. Both products can be separated chromatographically.

The formation of 1,2,4-trithiolanes of type **9** can occur via the [3+2] cycloadditions of either the thiocarbonyl *S*-sulfide of the hetaryl thioketone or the cycloaliphatic analogue. On the other hand, the formation of the dispiro-1,2,4-trithiolane **10** proves the appearance of the intermediate 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-sulfide. Aromatic thioketones are known as 'superdipolarophiles' and therefore, the first step of the reaction sequence is the [3+2] cycloaddition of benzyl azide (**2**) with the thioketone **1**. Additional evidence for this sequence is the absence of the products observed previously in the two-component reaction of **1c** with **2**.[19] For that reason, we propose that **1c** acts as a sulfur interceptor and generates the corresponding thiosulfine as a key intermediate. The latter reacts in competitive [3+2] cycloaddition with the hetaryl thioketone as well as with **1c**.

Hetaryl-substituted 1,2,4-trithiolanes are attractive substrates for coordination chemistry and their reactions with thiophilic Pt^0 complexes are of special interest.[20,21]

4. Experimental

4. 1. *General*

Melting points were determined in a capillary using a Melt-Temp. II (Aldrich) apparatus and are uncorrected. The IR spectra were recorded on a NEXUS FT-IR

spectrophotometer in KBr; absorptions in cm^{-1}. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III instrument (600 and 150 MHz, resp.) using solvent signals as reference. Chemical shifts (δ) are given in ppm and coupling constants *J* in Hz. All crude mixtures were separated by preparative TLC.

4. 2. *Starting materials*

Dihetaryl thioketones **1d** and **1e** were obtained in a typical manner from the corresponding ketones and Lawesson's reagent in boiling toluene or benzene,[14] whereas **1f** was prepared by treatment of *N*-methylpyrrol with thiophosgene in the presence of triethylamine.[22] 2,2,4,4-Tetramethyl-3-thioxo-cyclobutanone (**1c**) was prepared according to [23] by thionation of 2,2,4,4-tetramethylcyclobutane-1,3-dione with phosphorus pentasulfide in pyridine. Benzyl azide (**2**) was prepared from benzyl bromide and sodium azide according to a literature procedure.[24]

4. 3. *Two-component reaction of di(selenophen-2-yl) thioketone (1d) and benzyl azide (2)*

A solution of 152 mg (0.5 mmol) thioketone **1d** dissolved in excess benzyl azide (0.5 mL) was stirred magnetically and heated in an oil bath at 80 °C. After 4 h evolution of nitrogen ceased and excess benzyl azide was removed in vacuo (Kugel-Rohr apparatus, 0.2 Torr, 60 °C). The residual brownish oil was purified on preparative TLC plates (SiO_2, hexane/dichloromethane 1:1). The least polar fraction with R_f ca. 0.9 formed elemental sulfur, which hast not been isolated. The only fraction isolated from the plate (R_f ca. 0.5; 108 mg (75%)) was a colorless oil, which solidified at room temperature. Based on comparison of the ^{1}H NMR and IR spectra with an original sample it was identified as di(selenophen-2-yl) ketone (**8d**) [14].

4. 4. *Three-component reaction with dihetaryl thioketones 1, benzyl azide (2) and 2,2,4,4-tetramethyl-3-thioxo-cyclobutanone (1d) – general procedure*

A mixture of the corresponding thioketone **1d**−**f** (1 mmol), 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1c**, 0.5 mmol), benzyl azide (**2**, 1 mL) and a catalytic amount of $LiClO_4$ was heated in an oil bath at 60 °C. After 3 h excess of azide **2** was removed under reduced pressure. The obtained mixtures were purified by preparative TLC

(SiO_2), using as the eluent a mixture of petroleum ether and ethyl acetate (97:3) for **9a** and **9b** and a mixture of dichloromethane and petroleum ether (1:1) for **9c**. Products **9**, isolated as the less polar fraction, were additionally crystallized from diethyl ether. The more polar fraction was a mixture of the known dispiro compounds **10** [12] and the corresponding hetaryl ketones **8d–f**.[10]

1,1,3,3-Tetramethyl-7,7-di(selenophen-2-yl)-5,6,8-trithiaspiro[3.4]octan-2-one (**9a**)

Colorless crystals; yield: 217 mg (44%); m.p. 106−108 °C (diethyl ether). ^{1}H NMR: 1.48, 1.51 (2*s*, 12H, 4CH_3); 7.20 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 3.8 Hz, 2CH_{arom}); 7.34 (*dd*, $J_{H,H}$ = 3.8 Hz, $J_{H,H}$ = 0.6 Hz, 2CH_{arom}); 8.00 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 0.6 Hz, 2CH_{arom}). ^{13}C NMR: 21.3, 26.4 (4*C*H$_3$); 67.7 (2C_q(CH$_3$)$_2$); 84.0, 89.7 (2C_qS); 129.6, 130.8, 133.7 (6*C*H$_{arom}$); 154.5 (2C_{arom}); 218.0 (*C*=O). IR (KBr): 3087*m*, 2962*m*, 1787*vs* ($\nu_{C=O}$), 1636*m*, 1458*m*, 1378*m*, 1236*m*, 1227*m*, 1171*w*, 1026*m*, 922*m*, 820*m*, 709*s*, 688*vs*. Anal. calcd. for $C_{17}H_{18}OS_3Se_2$ (492.44): C 41.46, H 3.68, S 19.53; found: C 41.60, H 3.76, S 20.04.

1,1,3,3-Tetramethyl-7,7-bis(2-thienyl)-5,6,8-trithiaspiro[3.4]octan-2-one (**9b**)

Colorless crystals; yield: 200 mg (50%); m.p. 113–115 °C (diethyl ether). ^{1}H NMR: 1.47, 1.52 (2*s*, 12H, 4CH_3); 6.96 (*dd*, $J_{H,H}$ = 5.2 Hz, $J_{H,H}$ = 3.7 Hz, 2CH_{arom}); 7.15 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 1.1 Hz, 2C*H*arom); 8.00 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 0.6 Hz, 2CH_{arom}). ^{13}C NMR: 21.3, 26.3 (4*C*H$_3$); 67.6 (2C_q(CH$_3$)$_2$); 79.7, 89.5 (2C_qS); 126.7, 126.9, 128.6 (6*C*H$_{arom}$); 147.5 (2C_{arom}); 218.1 (*C*=O). IR (KBr): 3088*m*, 2963*s*, 1789*vs* ($\nu_{C=O}$), 1640*m*, 1459*s*, 1426*s*, 1378*m*, 1363*m*, 1237*s*, 1228*s*, 1170*m*, 1042*m*, 1027*m*, 922*m*, 857*m*, 817*m*, 775*m*, 753*m*, 716*s*, 700*vs*. Anal. calcd. for $C_{17}H_{18}OS_5$ (398.65): C 51.22, H 4.55, S 40.22; found: C 51.15, H 4.53, S 40.62.

1,1,3,3-Tetramethyl-7-(1-methylpyrrol-2-yl)-7-phenyl-5,6,8-trithiaspiro[3.4]octan-2-one (**9c**)

Colorless crystals; yield: 116 mg (30%); m.p. 120–122 °C (diethyl ether). ^{1}H NMR: 1.43, 1.48, 1.49, 1.55 (4*s*, 12H, 4CH_3); 3.25 (*s*, 3H, CH_3N); 6.07 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 2.8 Hz, 2CH_{arom}); 6.62 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 2.2 Hz, 2CH_{arom}); 6.67 (*br. t*, $J_{H,H}$ =

2.2 Hz, 2CH_{arom}); 7.28–7.33 (*m*, 3CH_{arom}); 7.49–7.51 (*m*, 2CH_{arom}). ^{13}C NMR: 21.2, 21.5, 26.0, 26.2 (4CH_3); 35.8 (CH_3N); 66.8, 67.7 (2C_q(CH_3)$_2$); 81.4, 89.1 (2C_qS); 105.8, 113.9, 125.5, 127.7, 128.2, 128.4 (6 signals for 8CH_{arom}); 131.1, 140.5 (2C_{arom}); 218.5 (*C*=O). IR (KBr): 2962*s*, 2923*m*, 1783*vs* ($\nu_{C=O}$), 1593*m*, 1487*m*, 1449*s*, 1438*s*, 1377*m*, 1360*m*, 1299*s*, 1233*m*, 1167*m*, 1093*m*, 1025*m*, 882*m*, 828*m*, 776*m*, 737*m*, 718*vs*, 702*s*. Anal. calcd. for $C_{20}H_{23}NOS_3$ (389.60): C 61.66, H 5.95, N 3.60, S 24.69; found: C 61.57, H 6.13, N 3.42, S 24.86.

4. 5. *X-ray crystal-structure determination of 9a*

All measurements were made on an Agilent Technologies SuperNova area-detector diffractometer [25] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) from a micro-focus X-ray source and an Oxford Instruments Cryojet XL cooler. Data reduction was performed with CrysAlisPro.[25]. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction using spherical harmonics [24] was applied. Equivalent reflections were merged. Data collection and refinement parameters are given below,[26] and a view of the molecule is shown in Figure 1. The structure was solved by direct methods using SHELXS-2013,[27] which revealed the positions of all non-H-atoms. The carbonyl group is disordered over two conformations. Two sets of positions were defined for the C- and O-atoms of the carbonyl group and the site occupation factor of the major conformation refined to 0.768(11). Similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered atoms, while corresponding atoms in the two conformations of the disordered carbonyl group were restrained to have similar atomic displacement parameters. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent C-atom (1.5U_{eq} for the methyl groups). The refinement of the structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_O^2-F_C^2)^2$. A correction for secondary extinction was not applied. Neutral atom scattering factors for non-H-atoms were taken from ref. [28], and the scattering factors for H-atoms were taken from ref. [29]. Anomalous dispersion effects were included in F_C;[30] the values for *f'* and *f''* were

those of ref. [31]. The values of the mass attenuation coefficients are those of ref. [32]. All calculations were performed using the SHELXL-2014 [33] program.

Crystal data for **9a**: $C_{17}H_{18}OS_3Se_2$, M = 492.31, crystallized from diethyl ether, colorless, prism, crystal dimensions 0.07 × 0.10 × 0.20 mm, triclinic, space group $P\bar{1}$, Z = 2, reflections for cell determination 12824, 2θ range for cell determination 5 – 61°, a = 6.67580(7) Å, b = 8.24707(11) Å, c = 18.08016(17) Å, α = 93.4135(9)°, β = 94.0158(8)°, γ = 106.2097(10)°, V = 950.243(19) Å^3, T = 160(1) K, D_X = 1.720 g·cm^{-3}, μ(MoK_α) = 4.219 mm^{-1}, scan type ω, $2\theta_{(max)}$ = 60.7°, transmission factors (min; max) = 0.714; 1.000, total reflections measured 23628, symmetry independent reflections 5239, reflections with $I > 2\sigma(I)$ 4584, reflections used in refinement 5239, parameters refined 231, restraints 19; $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0246, $wR(F^2)$ [all data] = 0.0575 (w = $[\sigma^2(F_o^2) + (0.0232P)^2 + 0.5336P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.055, final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min) = 0.47; –0.46 e Å^{-3}.

Acknowledgements

The authors thank Dr K. Urbaniak (University of Łódź) for her help in preparation of the manuscript.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the National Science Center (Cracow, Poland) within the project Maestro (Grant Number: Dec-2012/06/A/ST5/00219).

References

[1] Morita K, Kobayashi S. Isolation, structure, and synthesis of lenthionine and its analogs. Chem Pharm Bull 1967;15:988–993.

[2] Gmelin R, Susilo R, Fenwick GR. Cyclic polysulfides from *Parkia speciosa*. Phytochemistry. 1981;20:2521–2523.

[3] a) In *Flavor of Foods and Beverages. Chemistry and Technology*. Charalambous G, Inglett GE, Eds. Academic Press, Inc. London, 1978. b) Brinkman HW, Copier H, de Leuw JJM, Boen Tjan S. Components contributing to beef flavor. Analysis of the head space volatiles of beef broth. J Agr Food Chem. 1972;20:177–181.

[4] Shalaby EA, Nasr NF, El Sherief SM. An *in vitro* study of the antimicrobial and antioxidant efficacy of some natural essential oils. J Med Plants Res. 2011;5:922–931.

[5] Tjan SB, Haakman JC, Teunis CJ, Peer HG. Synthesis of 3,5-dialkyl-1,2,4-trithiolanes – Assignment of configuration and conformational analysis by PMR. Tetrahedron. 1972;28;3489–3500.

[6] Asinger F, Thiel M, Lipfert G, Synthese von 1,2,4-trithiolanen und 1,2,4,5-tetrathianen. Justus Liebigs Ann Chem. 1959;627,195–212.

[7] Mlostoń G, Heimgartner H, Thioaldehyde and thioketone *S*-sulfides (Thiosulfines). Science of Synthesis, Update 2014/2, Vol. 27, Schaumann E. Ed. Thieme, Stuttgart 2014, pp. 403–411.

[8] Huisgen R, Rapp J. Thiocarbonyl *S*-sulfides, a new class of 1,3-dipoles. J Am Chem Soc. 1987;109:902–903.

[9] Huisgen R, Rapp J. 1,3-Dipolar cycloadditions, 98 – The chemistry of thiocarbonyl *S*-sulfides. Tetrahedron 1997; 53: 939–960.

[10] Mlostoń, G, Romański J, Heimgartner H. Sulfur centered 1,3-dipoles. An efficient trapping of adamantanethione-*S*-sulfide generated in the reaction of adamantanethione with organic azides. Polish J Chem. 1996;70;437–445.

[11] Guziec Jr FS, Moustakis CA. Twofold extrusion reactions of selones and azides: the preparation of very sterically hindered imines. J Chem Soc Chem Commun. 1984;63–64.

[12] Mlostoń G, Heimgartner H. Formation of 1,2,4-trithiolanes in three-component reactions of phenyl azide, aromatic thiones, and 2,2,4,4-tetramethylcyclobutanethiones: A sulfur-transfer reaction in 'thiocarbonyl-thiolates' ((alkylidenesulfonio)thiolates) as reactive intermediates. Helv Chim Acta. 1995;78:1298–1310.

[13] Huisgen R, Mlostoń G, Polborn K, Palacios-Gambra F. Some cycloadditions of aromatic thione *S*-oxides. Liebigs Ann./Recueil 1997;187–192.

[14] Mlostoń G, Urbaniak K, Gębicki K, Grzelak P, Heimgartner H. Hetaryl thioketones: synthesis and selected reactions. Heteroatom Chem. 2014;25:548–555.

[15] Mlostoń G, Urbaniak K, Linden A, Heimgartner H. Selenophen-2-yl substituted thiocarbonyl ylides – at the borderline of dipolar and diradical reactivity. Helv Chim Acta. 2015;98:453-461.

[16] Mlostoń G, Pipiak P, Linden A, Heimgartner H. Studies on the reactions of thiocarbonyl *S*-methanides with hetaryl thioketones. Helv Chim Acta. 2015;98:462–473.

[17] Schönberg A, Urban W. Organic compounds of sulphur. Part XXV. The interaction between organic azides and aromatic thioketones and a new method of converting the azido-group into the amino-group. J Chem Soc. 1935;530–532.

[18] Johnson CK. *ORTEP II*, Report ORNL-5138, Oak Ridge National Laboratory: Oak Ridge, Tennessee, 1976.

[19] Mlostoń G, Romański J, Linden A, Heimgartner H. First example of an H-shift in 'thiocarbonyl amidines' (*N*-(alkylidenesulfonio)amidines). Helv Chim Acta. 1995;78:1067–1078.

[20] Weigand W, Bräutigam S, Mlostoń G. Selected cyclic oligosulfides and oligosulfide *S*-oxides and their reactions with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$. Coord Chem Rev. 2003;245:167–175.

[21] Petzold H, Weisheit T, Bräutigam S, Görls H, Mlostoń G, Weigand W. Reactions of 1,2,4-trithiolane and its 4-*S*-oxide with diphosphane Pt^o complexes. Eur J Inorg Chem. 2010;3636–3641.

[22] de Groot JA, Koek JH, Lugtenburg J. Synthesis and properties of 1,1′-methylene-2,2′-dipyrrolyl ketone. Recl Trav Chim Pays-Bas 1981;100:405–408.

[23] Elam EU, Davis HE, Chemistry of dimethylketene dimer. VII. Dimers of dimethylthioketene. J Org Chem. 1967;32:1562–1565.

[24] Ferreira MLG, Pinheiro LCS, Santos-Filho OA, Peçanha MDS, Sacramento CQ, Machado V, Ferreira VF, Souza TML, Boechat N. Design synthesis, and antiviral activity of new 1*H*-1,2,3-triazole nucleoside ribavirin analogs. Med Chem Res. 2014;23:1501–1511.

[25] *CrysAlisPro*, Version 1.171.37.31d, Agilent Technologies, Yarnton, Oxfordshire, England, 2014.

[26] CCDC-1416581 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

[27] Sheldrick GM. A short history of SHELX. Acta Crystallogr Sect A. 2008;64:112–122.

[28] Maslen EN, Fox AG, O'Keefe MA. in ‘International Tables for Crystallography’, Wilson AJC, Ed. Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, pp. 477–486.

[29] Stewart RF, Davidson ER, Simpson WT. Coherent X-ray scattering for the hydrogen atom in the hydrogen molecule. J Chem Phys. 1965;42:3175–3187.

[30] Ibers JA, Hamilton WC. Dispersion corrections and crystal structure refinements. Acta Crystallogr. 1964;17:781–782.

[31] Creagh DC, McAuley WJ. in 'International Tables for Crystallography', Wilson AJC, Ed. Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.6.8, pp. 219–222.

[32] Creagh DC, Hubbell JH. in 'International Tables for Crystallography', Wilson AJC, Ed. Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.4.3, pp. 200–206.

[33] Sheldrick GM. Crystal structure refinement with *SHELXL*. Acta Crystallogr Sect C. 2015;71:3–8.